FINAL REPORT

FOR CRADA NO. C-05-04

BETWEEN

BROOKHAVEN SCIENCE ASSOCIATES

AND

OXFORD INSTRUMENTS, INC.

Project Entitled: Manufacture of YBCO Superconducting Flexible Tapes from Nanoparticle Films Derived from Sedimentation and by Flame Deposition of Nanoparticles from Solution

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SUMMARY REPORT: MANUFACTURE OF YBCO SUPERCONDUCTING FLEXIBLE TAPES FROM NANOPARTICLE FILMS DERIVED FROM SEDIMENTATION

Abstract

The objective of this CRADA was to develop the experimental and theoretical basis of a technology to produce yttrium barium copper oxide (YBCO) superconducting flexible tapes derived from nanoparticle metal oxide sols. The CRADA was a joint effort between Oxford Superconducting Technology, Brookhaven National Laboratory and Karpov Institute of Physical Chemistry. The effort was divided into three main tasks, the synthesis of a heteroepitaxial oxide buffer layer, and the manufacture of a flexible biaxially textured metallic substrate and the synthesis of a heteroepitaxial crystalline YBCO layer.

The formation of a heteroepitaxial buffer layer was implemented using technology developed at the Karpov Institute of Physical Chemistry for the synthesis, stabilization and deposition of polymer stabilized nanoparticle metal oxide sols. Using this technology, flexible oriented RABiTS nickel tapes, manufactured and supplied by the CRADA partner, Oxford Superconducting Technology, Carteret, New Jersey, were coated with a film of metal oxide nanoparticles. After coating the RABiTS nickel tapes with the nanoparticle sols the nickel tape/nanoparticle composite structure was sintered in order to form a dense crystalline heteroepitaxial oxide layer on the surface of the tape, also known as a 'buffer' layer.

The final phase of the research was the formation of a heteroepitaxial YBCO layer, grown on top of the metal oxide buffer layer. This work was scheduled to follow the development of the heteroepitaxial oxide buffer layer as described above. Three different polymer stabilized sols, yttrium hydroxide, $Y(OH)_3$, copper hydroxide, $Cu(OH)_2$, and barium fluoride, BaF_2, were synthesized and combined in the appropriate stoichiometric ratio. This metal oxide sol was then be deposited onto the buffer layer and reacted to form a crystalline heteroepitaxial YBCO film ranging from 1–5 microns thick.

Introduction

The successful development of flexible YBCO superconducting tapes requires the integration of three technologies; 1) a flexible substrate with a high degree of crystalline texture, 2) an overlying metal oxide film, heteroepitaxial to the substrate, also known as a 'buffer layer' followed by 3) an overlying crystalline superconducting YBCO film, also heteroepitaxial with the buffer layer. In addition to successful integration, these technologies must be cost effective, that is, they must be economical. Efforts to develop a flexible textured substrate have already met with success. The 'RABITS' process, developed at Oak Ridge National Laboratory, uses the rolling and heat treating of nickel and nickel alloys to produce long lengths of highly textured nickel substrates approximately 100 microns thick. These substrates have been successfully used in the laboratory for the synthesis of YBCO tapes carrying critical currents in excess of 1 MA/cm^2. The flexible substrate that was supplied by the IPP industrial partner, Oxford Superconducting Technology, was manufactured using a variation of the RABITS process.

Buffer layers have been successfully deposited onto flexible substrates by three processes, sputtering, pulsed laser deposition (PLD) and flame deposition. While successful these techniques suffer from slow deposition rates, in some cases a few angstroms per second, and/or very high capital equipment costs.

YBCO heteroepitaxial films have been successfully deposited by a number of techniques but two, pulsed laser deposition (PLD) and the ex-situ BaF_2 process have received the bulk of development by the research and industrial community.

We chose the sedimentation of oxide nanoparticles as the method to be investigated for this new technology because it allows for the control of the chemical composition and surface structure of the initial oxide nanoparticles. The solution of other problems, for example, obtaining a sedimentary layer with a homogeneous nanostructure and a controllable thickness, demands the development of methods for control of the sedimentation process. For this purpose new highly specific copolymers, developed at the Karpov Institute, were introduced into oxide nanoparticle water sols in order to gain control of the change of the state of system from a sol to a suspension and back. By this technique a method for the production of a large area homogeneous sedimentary layers by the controllable deposition of one layer upon another was possible. Physical-chemical and mathematical models were developed for optimization of the processes of sedimentation (separation) and formation of the sedimentary layer.

Synthesis of the Heteroepitaxial Buffer Layer

The method for the production of both the heteroepitaxial oxide buffer layer and the YBCO precursor layer involved the introduction of specific thermo-responsive water-soluble polymers into nanoparticle water sols. The specific copolymers used in this project undergo a sharp reversible phase separation in water. The phase separation is due to a change in the polymer configuration from a chain to a globule and back depending on the temperature, polymer concentration, etc. Thus, by varying the temperature, polymer composition, polymer molecular weight and nanoparticle concentration we were able to control the process of sedimentation (separation) in a water sol suspension and, as a result, control the processes of formation of sedimentary nano-oxide polymer layers with a homogeneous microstructure.

The polymers used in this project were selected from the acrylamide family. These polymers undergo a sharp reversible phase separation in pure water in the temperature range 30-40^0C. These polymers are a water-soluble and temperature-dependent class of polymers whose molecular mass and composition can be varied over a wide range, which results in possibility of adaptively changing the conditions for sedimentation (separation) in water solutions.

The polymer most studied was poly-N-vinylcaprolactam (PVCL) and the PVCL used in this study had a molecular weight of about 10^6 atomic mass units. In pure water, at a concentration of about 0.1 – 1.0 weight percent, this polymer undergoes a phase transition in a temperature range of about 30 – 31 C. Below the phase transition temperature the polymer is extended in the form of a coil with a diameter of about 50 nanometers. Above the phase transition temperature the coils collapse and combine to form globules. These globules phase separate from the water solution forming a layer at the bottom of the vessel. The excess solution is discarded and the globule rich layer is dried, leaving behind a polymer nanoparticle layer or film.

Processing of RABiTS^{TM} Substrate at Oxford Superconducting Technology

The RABiTS substrate was originally developed at Oak Ridge National Laboratory [1]. The acronym RABiTS stands for rolling assisted biaxially textured substrate. It was well known that superconducting $Y_1Ba_2Cu_3O_7$ (YBCO) films with high critical currents exceeding $1x10^6$ amperes/cm^2 could be grown on single crystal oxide substrates such as $SrTiO_3$ or on metallic substrates coated with a suitable heteroepitaxial oxide surface layer, also known as a buffer layer.

It was also recognized that grain boundary misorientation in polycrystalline YBCO films greatly limited the obtainable critical currents. Generally speaking YBCO grain boundary angles of less than about 10^o are required to achieve critical currents exceeding 10^6 ampere/cm^2.

$Ni_{1-x}W_x$ materials with nominal compositions x = 3 or 5 atomic % W were used. Starting materials were procured in two forms. The first was rods that were produced by vacuum casting followed by hot rolling. The second was strip produced by powder metallurgy methods.

These starting materials were subjected to thermo-mechanical processing (a series of rolling deformations and heat treatment) to produce the desired (1 0 0) [1 0 0] cube texture, i.e., with one crystallographic {1 0 0} axis oriented perpendicular to the plane of the tape and with another directed along the tape axis. In the final step, the alloys were recrystallized by annealing at temperatures in the range T_{ann} = 900-1100 °C for the vacuum cast materials and 1000-1150 °C for the powder metallurgy alloys; the maximum temperature is limited by the need to avoid secondary recrystallization, which destroys the desired biaxial texturing.

Annealing of the tape was accomplished in a reel-to-reel fashion in a 5 m long tube furnace. The tape was pulled through a retort containing flowing forming gas (nitrogen with 5% hydrogen). The final anneal temperature was varied in an effort to obtain best biaxial texture. The speed of the tape through the furnace was varied to achieve the desired anneal time. The typical speed range was 5 to 20 cm per minute.

Two important aspects of the textured metal substrate are the quality of the biaxial texture (the extent to which the crystallographic axes of individual grains are aligned) and the surface smoothness. Both of these factors directly affect the critical current density that can be obtained in the subsequent superconducting coating. Both of these factors must be homogeneously maintained over long lengths of substrate in order to produce a quality superconducting tape.

Controlling the quality of the biaxial texture is a process that is only partially understood, and remains the subject of extensive research and development in those laboratories and companies that use this method of texture formation in coated superconductors. Some factors that are known to affect the final texture are purity of the starting alloys, the randomness of the alloy grain orientation distribution at the start of the thermo-mechanical processing, the grain size distribution in the starting material, the amount of total deformation applied, the temperature, time, and ambient atmosphere of the final recrystallization anneal. In this project, all of these factors were varied as part of the R&D efforts to improve biaxial texture.

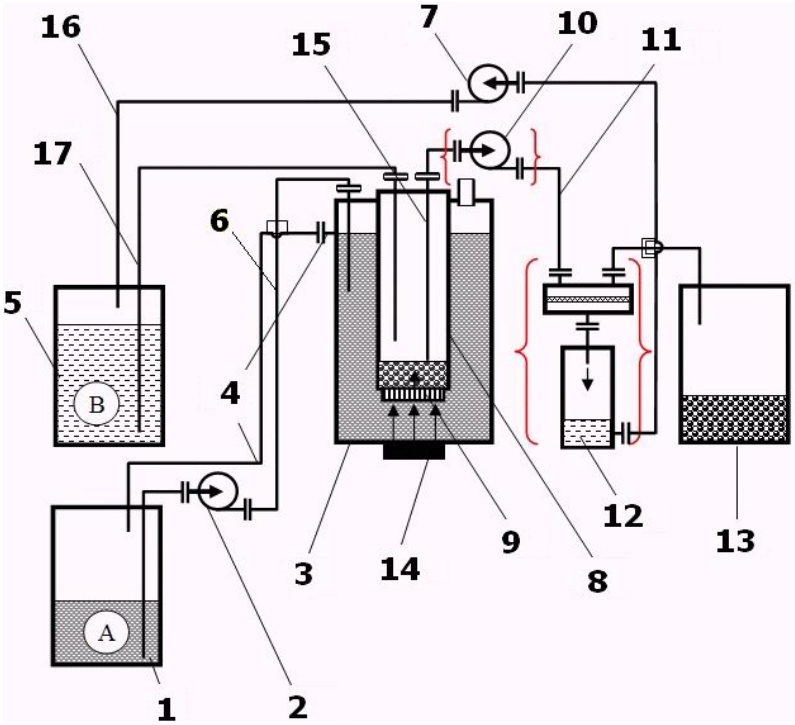
Controlling the surface smoothness of the substrate is done by ensuring the smoothness of the starting material, by controlling the smoothness of the tooling used in mechanical deformation, and in maintaining the cleanliness and absence of defects throughout the tape-processing path. In general, in the absence of dirt, scratches, or other defects in the processing path, the smoothness of the substrate tape corresponds closely to the smoothness of the work rolls used in the roll-deformation process. In this project, tungsten-carbide work rolls were used for the rolling deformation. The smoothness of the work rolls was maintained at approximately 25 nm RMS. The average surface smoothness of the final substrate was typically close to this value.

Synthesis of Nanoparticle Sols

As discussed earlier, the RABiTS nickel substrate requires a thin film coating of oxide buffer to prevent interaction with the $YBa_2Cu_3O_7$ (YBCO) superconductor. CeO_2, Y_2O_3, $SrRuO_3$, $SrTiO_3$ sols were chosen for investigation as oxide buffers. CuO, Y_2O_3, and BaF_2 sols were synthesized in order to deposit the YBCO superconductor. Metal alkoxides are widely used for

the synthesis of sols, powders and films. The advantage of their use consists in obtaining highly pure and homogeneous products and this method was chosen for the preparation of the oxide sols. The BaF_2 sol was obtained by extraction of a subset of BaF_2 nanoparticles. The initial solution of BaF_2 nanoparticles was obtained by mixing a BaF_2 commercial powder in water. After that the BaF_2 mixture was added to a water solution of PVCL. Next heating the PVCL water solution precipitated the largest BaF2 particles. The process was repeated; removing successively smaller BaF_2 nanoparticles until a BaF_2 sol with particles in the 8-20 nm size range was obtained.

To synthesize the necessary oxide nanoparticles, a new membrane-ultrasonic method was developed and is shown below;



The Membrane-ultrasonic method for obtaining nanoparticle sols is based on the use of ultrafiltration membranes, nuclear, polymer, or ceramic, for the dosed injection of one of reagents into the reaction zone. Although ultrafiltration membranes are permeable for electrolytes it is possible to stop penetration of one of the reagents through the membrane by the use of the second reagent under the required pressure on one side of the membrane. Equilibrium of the process of obtaining the required product can be achieved by simultaneous withdrawal of reaction product from reaction zone and injection of fresh reagent. The operation is as follows; A pump **2** pumps a solution of substance **A** from vessel **1** into an outer vessel **3**. After achieving a liquid column height determined by position of a connecting pipe **4**, excess liquid drains back in vessel **1**. Solution B substance from vessel **5** is transported into the inner zone of reactor **8** by vacuum created by a pump **10**. The solution level in the reactor is limited by position of pipe **15**. Solution **A** gets enters the inner zone of reactor **8** by micropores of a nuclear membrane **9** and reacts with solution **B**. As a result of this reaction, highly dispersed particles of solid substance

are formed in solution **B**. In order to avoid obstruction of the ultra filtration membrane channels, the reaction zone is exposed to a powerful ultrasonic radiation **14**, with intensity higher than the cavitation limit. The sol obtained is pumped by a pump **10** to a membrane concentrator **11**, where part of solution **B** is separated. Concentrated sol is collected in vessel **13** and solution **B** is pumped by a pump **7** back into vessel **5**.

Synthesis of CeO_2 Nanoparticle Sols

CeO_2 sols were the most studied system and were used to search for the optimum mode of the membrane ultrasonic set-up. Water solutions of NaOH (solution A) and cerium chloride $CeCl_36H_2O$ (solution B) were used as initial substances.

The following parameters were varied for the search of the mode of the set-up:

1) Concentration of solutions A and B was varied in the range from 0.005 M to 0.05 M;
2) Flow rate (consumption) was varied from 10 to 250 ml per min;
3) Cycle time was varied from 1 to 120 min;
4) Membrane pressure drop was varied from 0.5 to 5 cm of water column.

Nuclear and polymer membranes were used for the ultrafiltration. Polymer membranes were used in both hydrophilic and hydrophobic form. All membranes had pore dimensions of 30 nm. The products studied in membrane-ultrasonic set-up consisted of CeO_2 sols and the ion residues of initial solutions. Electrodialysis was used to remove these ions from the sol. The sols obtained were investigated by optical methods for the determination of the size of CeO_2 nanoparticles, for investigation of the effect of electrodialysis on particle size and for control of the complete removal of residue ions from the solution. More than 150 experiments were carried out in which the above-mentioned parameters were varied. Effect of concentrations of solutions A and B on the size of CeO_2 nanoparticles in the sol is shown in Table 1.

Table 1`

Concentration of NaOH (M)	**Size of CeO_2 particles (nm)** **The first designates the size of CeO_2 crystallites** **The second designates the size of aggregates** *** - the first and the second after electrodialysis**				
0,05	**8, 28, 8*, 25***	**8, 25, 8*, 29***	**7, 21 7*, 20***	**6, 18 6*, 20***	**6, 16 6*, 18***
0,03	**8, 29, 8*, 25***	**8, 25, 7*, 25***	**8, 25, 7*, 25***	**6, 19 5*, 19***	**6, 16 5*, 16***
0,02	**7, 21 7*, 20***	**7, 21 6*, 20***	**6, 20 5*, 19***	**6, 17 5*, 17***	**5, 15 5*, 19***
0,01	**6, 18 6*, 20***	**6, 19 5*, 19***	**6, 15 5*, 17***	**5,15, 5*, 16***	**4,14, 4*, 16***
0,005	**6, 16 6*, 18***	**6, 16 5*, 16***	**5, 16 5*, 17***	**4,14, 4*, 16***	**4,14, 4*, 16***
Concentration of $CeCl_36H_2O$ (M)	**0,05**	**0,03**	**0,02**	**0,01**	**0,005**

The first entry in Table 1 corresponds to the size of CeO_2 crystallites, i.e. nanoparticles that already possess the crystal structure of CeO_2. The size of these particles was determined from the

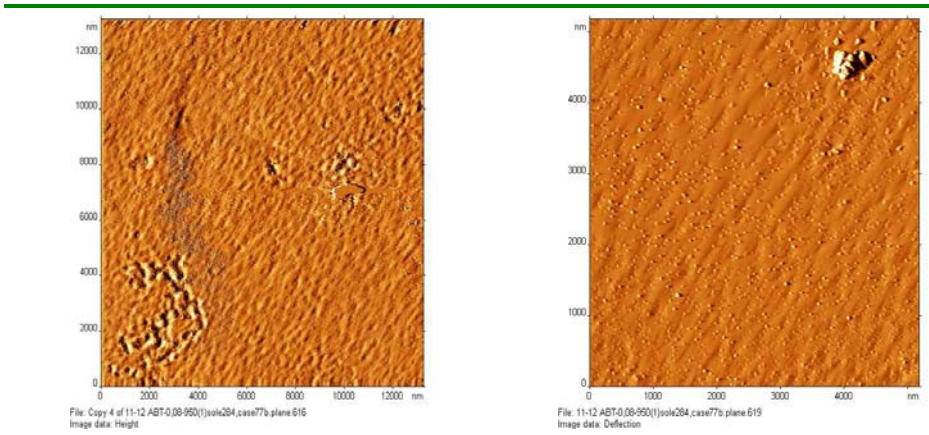
edge of the absorption band in UV region. Along with these particles, there are aggregates of CeO_2 crystallites in the fractal form and amorphous CeO_2 in the solution. The median size of such formations was estimated according to dispersion spectra in visible light, and this corresponds to the second entry in Table 1. Figures marked with stars correspond to analogous data obtained for sols after electrodialysis. According to Table 1, the dispersability of CeO_2 sols depends on the initial concentration of the A and B solutions. By convention, Table 1 can be divided in three zones that correspond to the values of the median sizes of CeO_2 crystallites and fractals (aggregates). The first zone corresponds to concentrations of the initial $CeCl_36H_2O$ and NaOH solutions in the range from 0.05 M to 0.02 M. The median size of CeO_2 crystallites is of 7-8 nm and the median fractal size is of 28-21 nm. The median size of CeO_2 crystallites in the second zone is of 7-8 nm; the median fractal size is of 28-21 nm. This zone includes products obtained from the initial $CeCl_36H_2O$ and NaOH solutions with concentration lying in the whole concentration range tested, except when concentrations of both solutions were equal in the areas of high and low concentrations. In the third zone the median CeO_2 crystallite size is 4-5 nm and the median fractal size is of 14-17 nm. Concentrations of the initial $CeCl_36H_2O$ and NaOH solutions were in the range from 0.02 M to 0. 005 M.

According to the results in Table 1, the electrodialysis of products of membrane-ultrasonic synthesis has no effect on the median size of CeO_2 crystallites and their aggregates.

It has been shown that the rate of solution B flow, the pressure drop and the cycle time have an influence on the size of nanoparticles synthesized.

The CeO_2-polymer sols were synthesized and a three-stage sedimentation process was developed. CeO_2-PVCL films were deposited by sedimentation onto a nickel substrate and the polymer was 'burned-off' by heating the films in air at temperatures of 300-450 C. The films were then annealed at high temperature in an attempt to crystallize the CeO_2 nanoparticles and form a heteroepitaxial structure. AFM scans at two different magnifications are shown in Figures 1 and 2.

Figure 1 **Figure 2**



The x-ray diffraction scan of the CeO2-nickel composite film of Figures 1 and 2 is shown below in Figure 3.

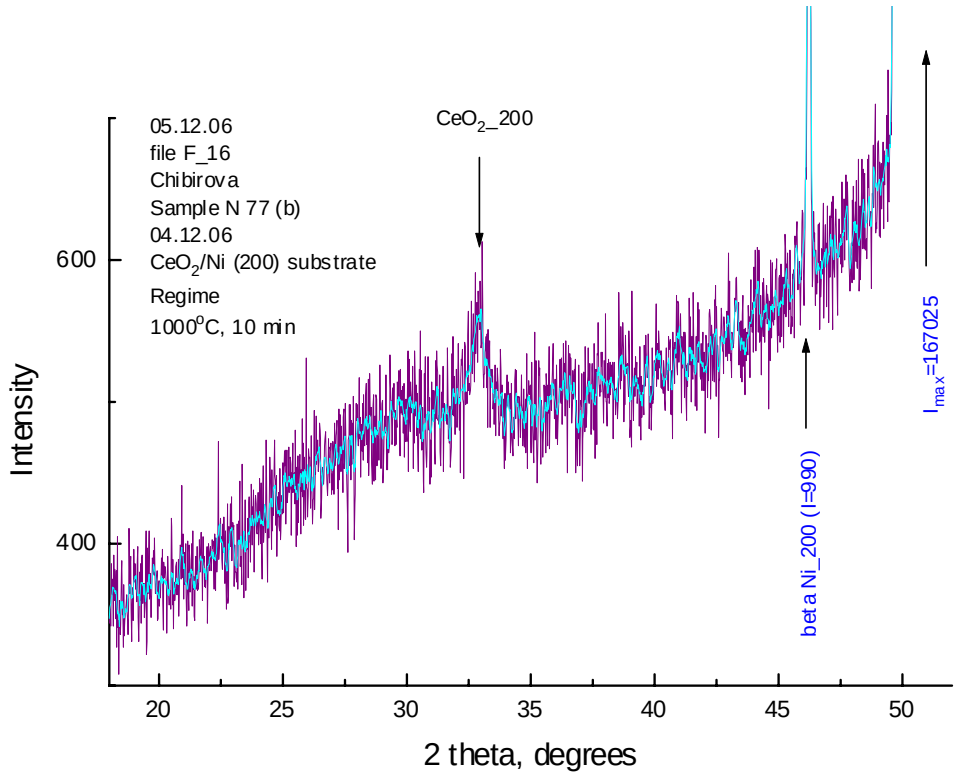


Figure 3

The other oxide buffer layer materials, Y_2O_3, $SrRuO_3$, and $SrTiO_3$, were synthesized using similar techniques.

Synthesis of $Cu(OH)_2$ and $Y(OH)_3$ sols

Membrane-ultrasonic synthesis of $Cu(OH)_2$ and $Y(OH)_3$ sols was based on the experience gained during the syntheses of CeO_2 sols. Analogous to the synthesis of the CeO_2 sols, copper chloride, $CuCl_2$, and yttrium chloride, YCl_3, were chosen for the A solutions and NaOH was chosen for the B solution.

Experiments studying the effect of the concentration of the A and B solutions A and B on the size of the nanoparticles of $Cu(OH)_2$ and $Y(OH)_3$ sols were carried out. Experimental conditions were similar as for the synthesis of the CeO_2 sols. The concentration of A and B solutions ranged from 0.05 to 0.005 M. The flow rate of 100 ml per min and the pressure drop was 2 cm of water column.

The sizes of the nanoparticles of $Cu(OH)_2$ and $Y(OH)_3$ sols obtained in the first experiments are given in Tables 2 and 3.

Analysis of these results shows that the conditions of synthesis are satisfactory for $Y(OH)_3$ sols (Table 3). Sizes of particles in these sols change with the change of concentration of solutions A and B in the range from 48 nm (0.05M YCl_3 and 0.05M NaOH) to 9 nm (0.005M YCl_3 and 0.005M NaOH). As for the synthesis $Cu(OH)_2$ sols, Table 2, the sizes of the $Cu(OH)_2$

particles in the sols are rather large, from 95 to 23 nm, and in there is no regularity in size, characteristic of previous experiments involving the synthesis of $Y(OH)_3$ and CeO_2 sols. The size of the particles of the $Cu(OH)_2$ sols is not dependent of the concentrations of the initial reagents. However, close inspection of these data shows that the size of $Cu(OH)_2$ particles is more dependent of the concentration of the NaOH solution than of the concentration of the $CuCl_2$ salt. This could be due to the mechanism of formation of $Cu(OH)_2$ sols, the pressure drop at the membrane or the concentration of alkali in the reaction solution.

In any case, it is possible to use the membrane-ultrasonic method of synthesis for obtaining $Cu(OH)_2$ and $Y(OH)_3$ sols.

Table 2

Concentration of NaOH (M)	**Size of $Cu(OH)_2$ particles (nm)**				
0,05	**95**	**90**	**81**	**69**	**55**
0,03	**83**	**70**	**63**	**54**	**48**
0,02	**70**	**65**	**51**	**44**	**40**
0,01	**51**	**53**	**45**	**39**	**35**
0,005	**43**	**39**	**33**	**27**	**23**
Concentration of $CuCl_2$ (M)	**0,05**	**0,03**	**0,02**	**0,01**	**0,005**

Table 3

Concentration of NaOH (M)	**Size of $Y(OH)_3$ particles (nm)**				
0,05	**48**	**46**	**39**	**29**	**22**
0,03	**48**	**43**	**37**	**25**	**17**
0,02	**35**	**33**	**29**	**21**	**14**
0,01	**27**	**27**	**24**	**15**	**12**
0,005	**20**	**16**	**11**	**9**	**9**
Concentration of YCl_3 (M)	**0,05**	**0,03**	**0,02**	**0,01**	**0,005**

All these sols were tested for use in the synthesis of YBCO films.

Tricomponent sol obtained by mixing stoichiometric ratios of $Y(OH)_3$, $Cu(OH)_2$ and BaF_2 sols

Initial tricomponent stoichiometric $Y(OH)_3$, $Cu(OH)_2$ and BaF_2 sols were compounded as follows; $Y(OH)_3$ was synthesized in a water solution of polymer with a limited distribution of the size of nanoparticles from 5-9 nm. $Cu(OH)_2$ was stabilized with a polymer with a medium size of nanoparticles 10-15 nm. Finally, a BaF_2 sol was obtained by the successive polymer

extraction of a smaller fraction of nanoparticles from an initial powder of nanoparticles in water until a BaF_2 sol with the size of BaF_2 particles of 8-20 nm was obtained. Later in the project BaO_2 sols were substituted for the BaF_2 sols.

Typical results are presented below. An oriented Ni-W substrate was coated with two $SrTiO_3$ buffer layers each 20 nm thick. Next two layers of a tricomponent sol consisting $Y(OH)_3$ + BaO_2 + $Cu(OH)_2$ were applied. The heat treatment for the tricomponent sol was as follows;

150^0C for 15 min in Ar (50 cm^3/min)
400^0C for 5 min in N_2 (50 cm^3/min)
930^0C for 180 min in Ar + H_2O (100 cm^3/min)
Sample furnace cooled in Ar (100 cm^3/min) to 600^0C
600^0C for 30 min in N_2 (30 cm^3/min)
Sample furnace cooled to RT in Ar (50 cm^3/min)

AFM scans of the film at two different magnifications are shown in Figures 4 and 5.

Figure 4

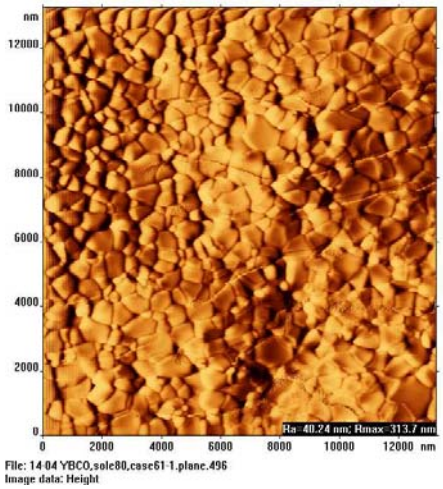
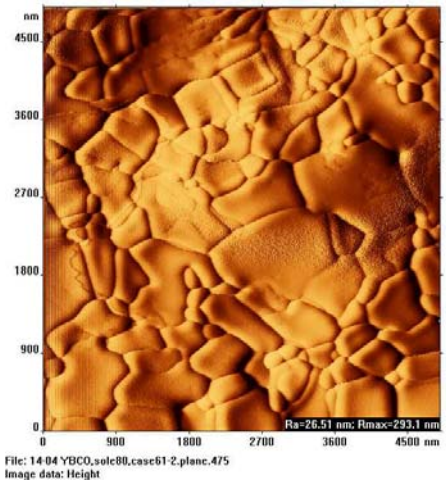


Figure 5



The x-ray diffraction scan of the composite film of Figures 4 and 5 is shown below in Figure 6.

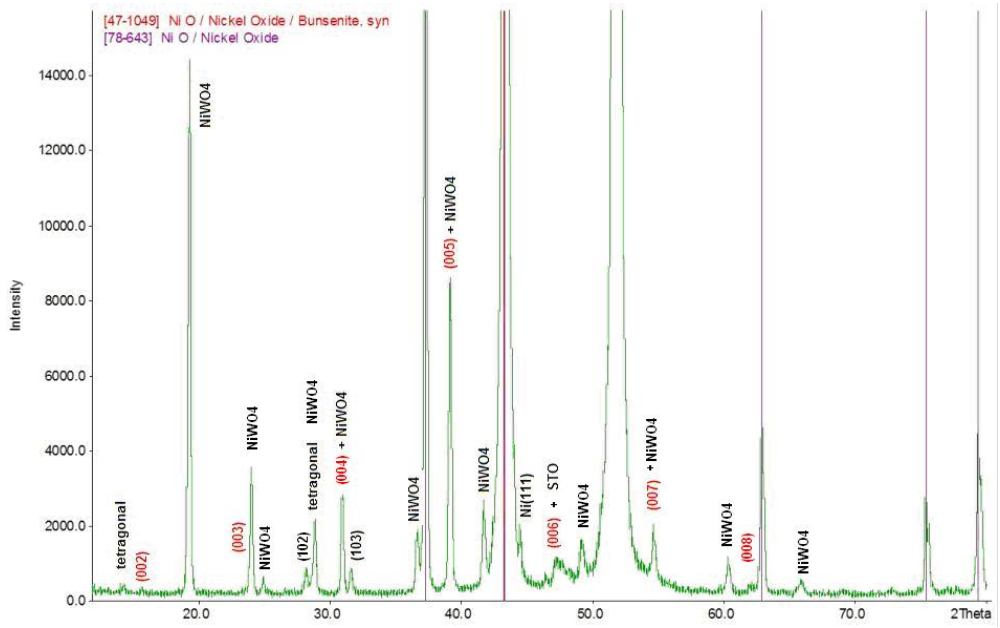


Figure 6: Xray Spectrum of Film in Figs 4 and 5

The film consists of flat grains of the predominantly rectangular form tightly pressed to each other and forming a solid coating. In the area of the plate boundaries small formations of a round form occur. Along with intensive lines of nickel, its oxides, and nickel tungstate, the X-ray spectrum of the sample contains the whole series of the superconducting YBCO phase lines as well as lines of the tetragonal phase. However, the amount of this phase is much less than that of the superconducting $YBa_2Cu_3O_7$ phases.

Conclusions

During the course of this project the following results were achieved:

I. The laboratory equipment for the deposition of precursor nanoparticle-polymer layers onto Ni-W substrates was designed and manufactured;

II. Methods for the production of nanoparticle sols of CuO, CeO_2, Y_2O_3, $SrRuO_3$, $SrTiO_3$, and BaF_2 in water polymer solutions were investigated;

III. The techniques of controllable sedimentation of precursor layers of epitaxial CeO_2, Y_2O_3, $SrRuO_3$, $SrTiO_3$, YBCO films were developed;

IV. The technology for the formation of epitaxial buffer layers on oriented Ni-W substrates derived from precursor nanoparticle-polymer layers were developed including:

1) Epitaxial CeO_2 buffer layers,
2) Epitaxial $SrTiO_3$ buffer layers,
3) Epitaxial $SrRuO_3$ buffer layers,
4) Epitaxial Y_2O_3 buffer layers;

V. The technology for epitaxial YBCO film formation on oxide buffer layers from stoichiometric homogeneous precursor layers was studied.